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by Frank C. De Lucia Jr. and Jennifer L. Gottfried

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**Frank C. De Lucia Jr. and Jennifer L. Gottfried
Weapons and Materials Research Directorate, ARL**

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Classification of explosive residues on organic substrates using laser induced breakdown spectroscopy

Frank C. De Lucia, Jr.,* and Jennifer L. Gottfried

U.S. Army Research Laboratory, RDRL-WML-A, Aberdeen Proving Ground, Maryland 21005, USA

*Corresponding author: frank.c.delucia.civ@mail.mil

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Standoff laser induced breakdown spectroscopy (LIBS) has previously been used to classify trace residues as either hazardous (explosives, biological, etc.) or benign. Correct classification can become more difficult depending on the surface/substrate underneath the residue due to variations in the laser-material interaction. In addition, classification can become problematic if the substrate material has a similar elemental composition to the residue. We have evaluated coupling multivariate analysis with standoff LIBS to determine the effectiveness of classifying thin explosive residue layers on painted surfaces. Good classification results were obtained despite the fact that the painted surface contributes to the LIBS emission signal. © 2012 Optical Society of America

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1. Introduction

At the U.S. Army Research Laboratory (ARL), we have been using laser induced breakdown spectroscopy (LIBS), an optical spectroscopic technique that determines the elemental composition from the light emission of a laser-generated microplasma, to classify trace residues at standoff distances as either hazardous or nonhazardous. LIBS is an ideal technique for standoff residue analysis since no sample preparation is required and only a small amount of material (nanograms-picograms) is needed to generate a usable atomic emission spectrum [1,2]. Since LIBS is an all optical technique and the instrumentation involves simple components, it can be configured for standoff measurements [3–7]. LIBS has been previously evaluated as a technique to characterize hazardous residues, including explosives [8–13]. The coupling of LIBS with multivariate analysis has been used for numerous applications. In particular, partial least squares discriminant analysis (PLS-DA)

coupled with LIBS spectral information is a powerful tool for producing robust classification models [14–18]. We have obtained good results classifying explosive and non-explosive residues in the laboratory and at standoff distances using PLS-DA [19,20]. In the majority of these experiments, the underlying substrate has been aluminum. In one case, we investigated a set of residue samples consisting of an explosive and two background materials, dust, and oil, on different substrates such as wood, clay tile, steel, rubber, aluminum, and silicone [21]. Good classification results were obtained for the majority of the samples; however there were some substrates that had high false positive rates such as the wood, travertine, and steel. Different substrates will alter the light emission from the microplasma due to the complex nonlinear processes associated with the laser-material interaction that initiates plasma formation. Thus, the LIBS spectrum collected from a residue on one type of substrate may differ significantly from the LIBS spectrum collected from the same residue on a different substrate, making correct classification difficult.

Another challenge for classification is if the substrate composition is similar to the composition of

the residue, since light from the microplasma will indiscriminately include emission from the residue and the substrate. The design of an effective classification model becomes difficult with an increasing diversity of samples and substrates. For this paper, we used the ARL standoff LIBS system to collect an extensive set of LIBS spectra that included multiple types of explosives and background interferent residues dispersed on painted metal surfaces of different colors. The composition of the painted surface varies from paint color to paint color, but all of the painted surfaces will have organic components. The LIBS signal includes carbon, hydrogen, nitrogen, and oxygen atomic emission from the organic residues as well as from the painted substrates. Data from the LIBS spectra were used to construct several PLS-DA models with the goal to classify samples as either an explosive or a nonexplosive irrespective of the substrate composition.

2. Experimental

We obtained the explosive samples of cyclotrimethylenetrinitramine (RDX), trinitrotoluene (TNT), and Composition-B (36% TNT, 63% RDX, and 1% wax) from colleagues at ARL. The car panels were obtained from the following vehicles at a junkyard: 1998 black Ford pickup, 1993 white Honda Accord EX, 1993 teal Jetta, 1991 metallic blue Toyota pickup, 1987 dark green Mazda pickup, 1986 silver Volvo 740 GL, and a 1985 red Toyota pickup. In addition, a second black car panel and a light green car panel were obtained from unknown vehicles. Circular discs about 6–8 inches in diameter were removed from the car panel to use as substrates to be interrogated by the standoff LIBS system.

Explosive residue samples were prepared by applying a small amount (~1–2 mg) onto the car panel and then crushing the explosive and smearing it over the entire panel. Loose explosive particles were brushed or knocked off the car panel. Typical coverage is estimated to be ~10 $\mu\text{g}/\text{cm}^2$ once the excess explosive is removed. Non-explosive samples include Arizona road dust, sand, diesel fuel, lubricant oil, fingerprint oil, and blank (no residue) car panels. Arizona road dust and sand were added in a similar manner as the explosives, but the coverage was not determined. Diesel fuel and lubricant oil were spread onto the surface and then wiped down with a cloth, leaving behind a minimal amount of coverage. No estimation of the coverage was determined for fuel or oil. Fingerprint oil was applied by handling the car panel and pressing fingertips repeatedly across the surface of the car panel.

All of the PLS-DA analysis was performed using the PLS_Toolbox version 5.0 (Eigenvector Technologies, Inc.) running under Matlab version 7.5 (Mathworks). Variable importance in projection (VIP) scores were also calculated using the PLS_Toolbox. PLS-DA is a supervised multivariate inverse least squares discrimination method that generates predictor variables (latent variables, LV) used to classify

samples [22]. The goal of PLS-DA is to find the maximum separation between each class, not the overall variance of the data set. In test sets where intraclass variance approaches interclass variance, discrimination between groups is more difficult to achieve using techniques that maximize overall variance.

For these experiments, we collected single-shot LIBS spectra of residues on the various car panels. The spectra were divided into two groups, one for training the model and the other for validating the model. We used either the whole broadband spectrum or particular atomic emission line intensities and atomic emission line ratios of interest as input variables. The output of the PLS-DA models returns the probability that a sample belongs to a particular class, in this case an explosive class or a non-explosive class. Samples that have at least a 75% probability of belonging to a class were considered part of the class.

The standoff LIBS system used for these experiments, shown in Fig. 1, employed a double-pulse laser source (Quantel Brilliant Twins, 1064 nm, 10 Hz, 250 mJ/pulse, 5 ns pulse width) that provided a laser beam with a $M^2 < 2$ at 20+ meters. The area interrogated by the laser is estimated to be about 5 mm². A 14" telescope (Meade LX200GPS) was fitted with UV-coated optics to provide full broadband (UV-VIS-NIR) capability. A custom-made three-channel gated CCD spectrometer (Ocean Optics) with adjustable gate width provides light throughput and sensitivity from 190–840 nm. We used a gate width of 800 μs in order to ensure all of the emission was collected.

The optimum timing for collecting LIBS spectra from the car panel surface was determined by collecting multiple LIBS spectra of a silver car panel, RDX on a silver car panel, and lubricant oil on a silver car



Fig. 1. (Color online) Standoff LIBS system.

panel at 30 meters at various gate delay times (500 ns, 1 μ s, 2 μ s) and interpulse delays (500 ns, 1 μ s, 2 μ s, 3 μ s, 5 μ s). In order to avoid damaging optical components in the standoff system we did not investigate interpulse delays less than 500 ns. Two parameters were used to determine the optimal timing: the signal-to-noise ratio (SNR) of the atomic emission intensities of the RDX (carbon, hydrogen, nitrogen, and oxygen) on the silver car panel and the root-mean-square error of calibration (RMSEC) for the PLS-DA model. The RMSEC is a measure of how well a model fits the data. A lower RMSEC value indicates the model fits the data better. In this case, a PLS-DA model was built containing three classes: explosive residue on a car panel, a car panel blank, and oil on a car panel. The PLS-DA model determines the maximum variance between each class. The model with the highest variance between the classes will yield the lowest RMSEC value. In Fig. 2, two contour plots that graph the sum total of the C, H, N, and O

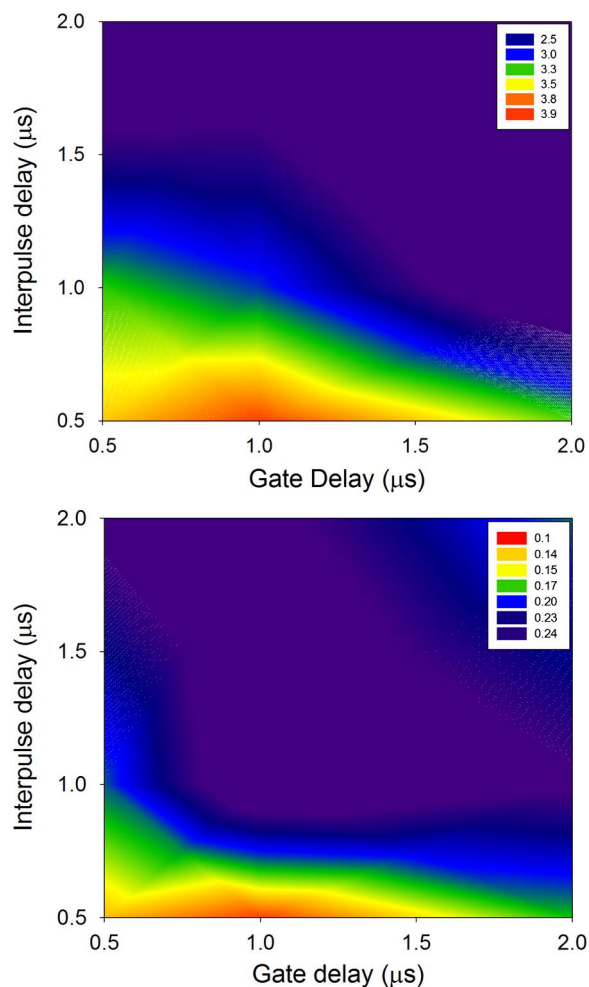


Fig. 2. (Color online) Timing optimization of double-pulse standoff LIBS system at 25–30 meters. Top: SNR of carbon, hydrogen, nitrogen, and oxygen of RDX on silver car panel at various gate delays and interpulse delays. Bottom: RMSEC value of a model containing RDX on a silver car panel, oil on a silver car panel, and a blank silver car panel. For both cases the best timing is a 1 μ s gate delay and a 0.5 μ s interpulse delay.

atomic emission line SNR (top) and the RMSEC (bottom) versus the interpulse delay and the gate delay are shown. The optimal SNR and RMSEC values occur at an interpulse delay of 500 ns and a gate delay of 1 μ s. These values were used for collecting all of the LIBS spectra.

3. Results

A. Classification of Painted Surfaces

For our initial standoff tests, we collected multiple LIBS spectra of each car panel color (99 black, 100 blue, 100 green, 110 silver, 100 teal, 100 white, and 99 red) at 25 and 30 meters. In Fig. 3, the LIBS spectra of each color car panel are displayed. Some of the car panel spectra are easy to differentiate, such as the white car panel, which has strong titanium emission between 300–350 nm. Others are harder to differentiate, such as the black car panel and the blue car panel. The car panel spectra were divided into two sets, a training set and a validation set shown in Table 1. A PLS-DA model was constructed using the entire LIBS spectrum as the variable input for each car panel sample. The model contains seven classes; each class corresponds to a different color. The root-mean-square error of cross-validation (RMSECV) was calculated for a range of latent variables in order to determine the model's ability to correctly classify samples not used to train the model. The RMSECV shows that the optimal model has 40 latent variables. The optimal model was used to classify the samples in the validation set. For our tests, a test sample is considered classified correctly if it has 75% or greater probability of belonging to the correct model class and does not have a 75% or greater probability for belonging to any of the other classes. A sample is considered misclassified if it has a 75% or greater probability of belonging to one of the six incorrect classes. A sample is considered unclassified if it has a 75% or greater probability of belonging to two or more classes (or none of the classes). As shown in Table 1, the PLS-DA model correctly classifies the test samples at a 98% rate with no misclassified samples and a 2% unclassified rate.

The VIP scores of each class were used to determine how much each variable in the model contributed to the classification. In Fig. 4, the VIP scores of the white car panel class and the black car panel class are compared. As expected the atomic emission due to titanium from 300–350 nm is important for the white car panel classification. Atomic emission due to aluminum (396 nm), sodium (589 nm), and hydrogen (656 nm) is more important for the black car panel classification than the white car panel. The VIP scores indicate that the seven car panel colors can be distinguished from each other based on their elemental composition.

B. Classification of Residues on Car Panels

We applied the RDX, TNT, lubricant oil, dust, fingerprint oil, and sand to the car panels and collected

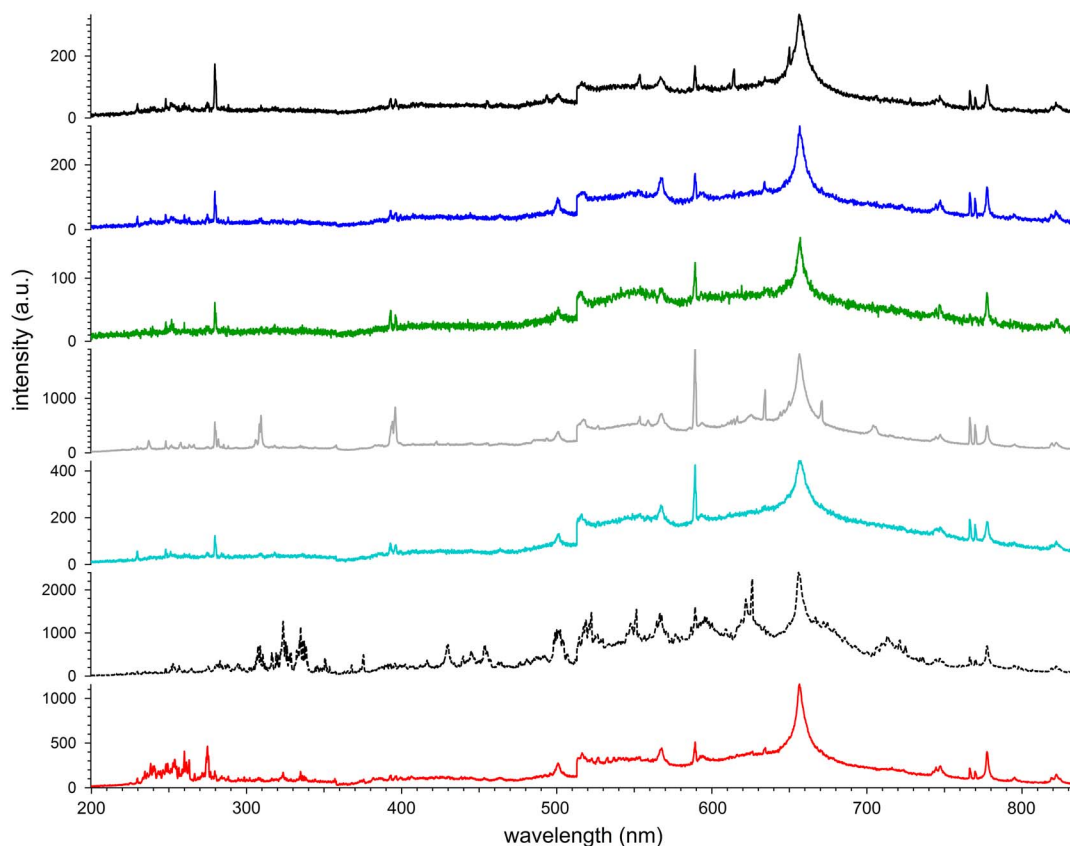


Fig. 3. (Color online) LIBS spectra of car panels. From top: black, blue, dark green, silver, teal, white, and red.

LIBS spectra at standoff distances of 25–30 meters. LIBS spectra of RDX, lubricant oil, and dust on a dark green car panel and a blank dark green car panel are displayed in Fig. 5. The RDX residue and the blank car panel share atomic emission lines due to carbon (247 nm), hydrogen (656 nm), nitrogen (746 nm), and oxygen (777 nm). There are noticeable differences among the spectra due to the elemental composition of the residues and the overall background intensity; in particular, the presence of any residue on the car panel increases the overall spectral emission since the clearcoat on the car panels results in poorer laser-material interaction. In Fig. 6, LIBS spectra of RDX residue on a black, red, teal, and white car panel and the blank of each color are displayed. The background emission in the RDX residue spectra is stronger than the blank for each car

panel. The relative nitrogen and oxygen atomic emission intensity at 746 and 777 nm is also stronger in the RDX residue spectra.

A PLS-DA model was built that included LIBS spectra of each residue on each car panel color in order to classify unknown residues as an explosive or non-explosive. In Table 2, the 414 LIBS spectra collected for the model from residues on black, blue, dark green, silver, teal, red, and white car panels are listed. The broadband spectra of each sample were used as the variable inputs for the model. The spectra were grouped as a class based on the residue type on the car panel rather than the color of the car panel. For example, the lubricant oil class in the model contained 10 samples from each of the seven car panel colors for a total of 70 samples. The model contained six classes of residues on car panels:

Table 1. Number of Spectra in Training and Validation Sets for Classifying Car Panels Based on Car Color and the Classification Results

Car Panel	# in Training Set	# in Validation Set	Test Samples Classified Correctly	Test Samples Misclassified	Test Samples Unclassified
Black	69	30	97%	0%	3%
Blue	70	30	93%	0%	7%
Dark Green	70	30	97%	0%	3%
Silver	77	33	100%	0%	0%
Teal	70	30	100%	0%	0%
Red	69	30	100%	0%	0%
White	70	30	100%	0%	0%
All	495	213	98%	0%	2%

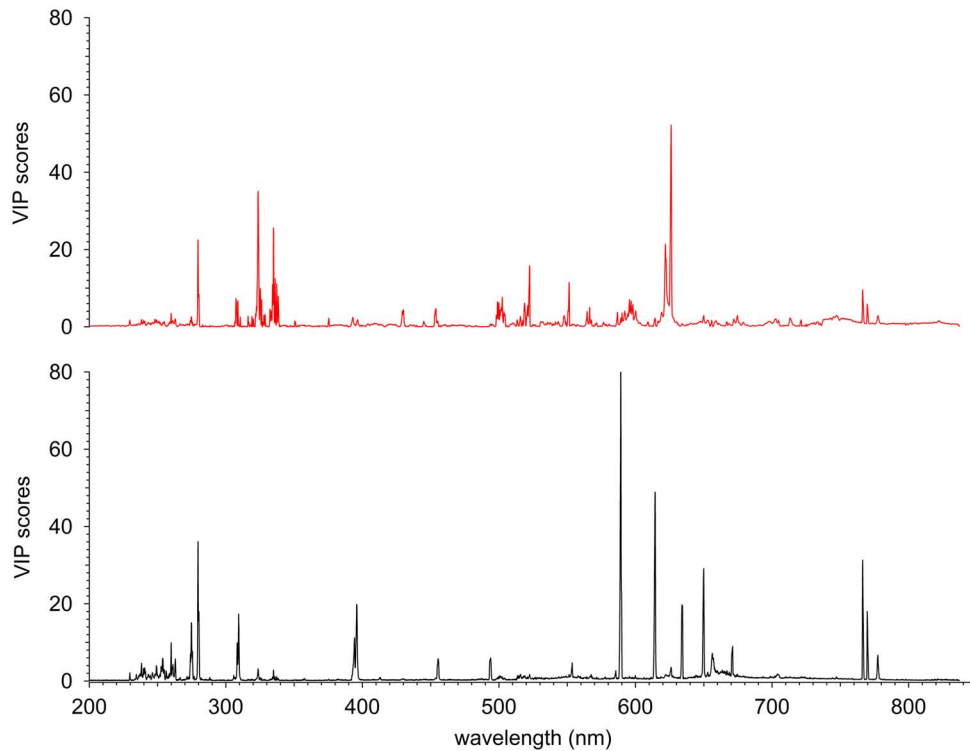


Fig. 4. (Color online) VIP scores of white car panel class (top) compared to the black car panel class (bottom) from the PLS-DA car panel model.

explosive (TNT and RDX), blank car panel, lubricant oil, dust, fingerprint oil, and sand. By defining the classes of the model by residue and not by color of the car panel, the PLS-DA model maximized the variances between the residues instead of the substrates. The optimal number of latent variables for the whole spectra PLS-DA model was determined to be 70 based on the cross-validation (CV) classification error, RMSECV, and RMSEC.

We collected another 850 LIBS spectra of residues on black, blue, dark green, silver, teal, red, and white car panels to test against the whole spectra model, and they are listed in Table 2. For each test sample, the probability that the sample belongs to the explosive class was calculated from the PLS-DA model and classification was determined using the same criteria outlined above. A true positive rate (TPR) of 99.5% for 210 explosive test samples and a false positive

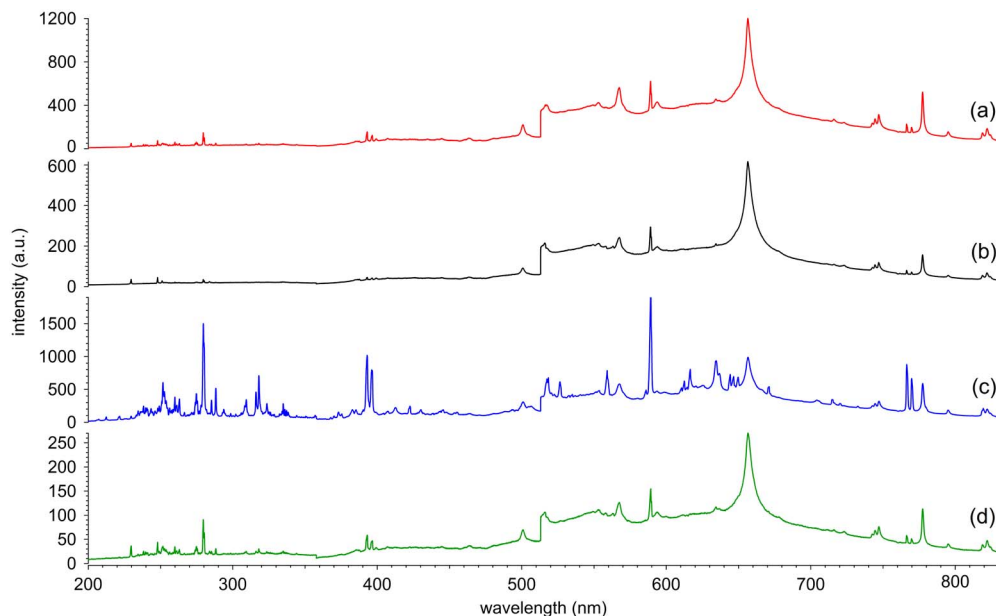


Fig. 5. (Color online) LIBS spectra of (a) RDX on dark green car panel, (b) lubricant oil on dark green car panel, (c) dust on dark green car panel, and (d) blank dark green car panel. Note the different y axis scale for each spectrum.

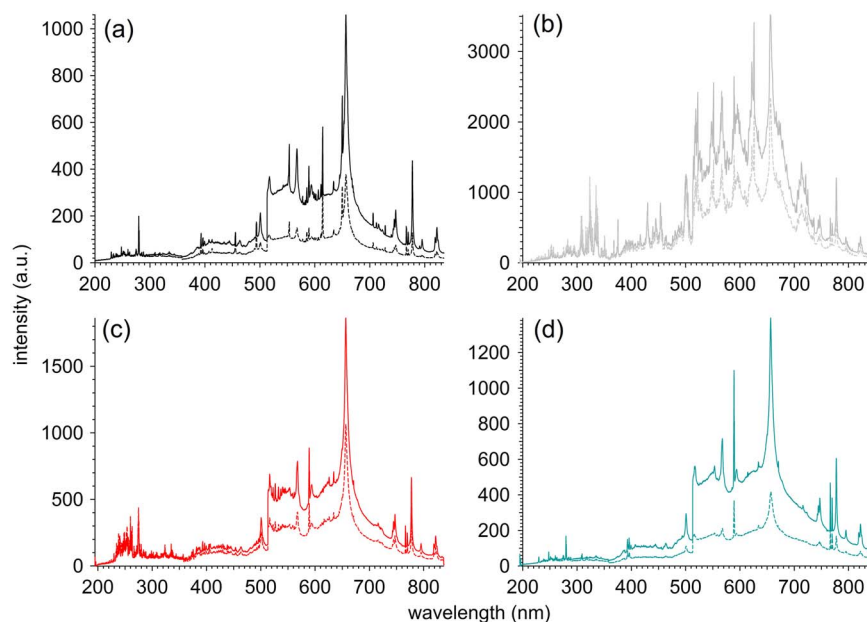


Fig. 6. (Color online) LIBS spectra of RDX residue on car panel (solid) and blank car panel (dashed) for (a) black, (b) white, (c) red, and (d) teal car panels.

rate (FPR) of 1.9% for 640 non-explosive test samples were calculated using the whole spectra PLS-DA model. We used the VIP scores to determine the variables that contributed to the explosive classification. In Fig. 7, the VIP scores of the explosive class are compared to the LIBS spectra of RDX on a car panel and a blank panel. All four constituent elements of RDX (C, H, N, and O) contribute to the explosive classification. However, there are other variables that contribute to the separation of the explosive class from the non-explosive classes; these include but are not limited to silicon (251 and 288 nm), magnesium (279 nm), aluminum (309 and 394 nm), titanium (320–340 nm), and potassium (766 and 769 nm). This indicates that classification is partly based on the background substrate composition and not just the residue composition.

Since the goal is to separate explosives from non-explosives, the data set can be down-selected *a priori*, in this case from the broadband spectrum to the atomic emission intensities of interest. We selected emission intensities associated with the constituent

elements of the explosive samples, i.e., C, H, N, and O and the molecular emissions due to C_2 (516 nm), and CN (388 nm). Previously, we had used nonlinear combinations of the normalized emission intensities of the constituent elements and molecular species to describe the plasma chemistry of the sample as variable inputs for a PLS-DA model [23]. The variable inputs, which include summed intensities of multiple emission lines from the same species (“sum”) and intensities normalized to the total emission intensity (“norm”), are listed in Table 3.

Using the 132 down-selected variable inputs, a PLS-DA model similar to the whole spectra model was constructed. It contained six classes based on residue type: explosive, blank, lubricant oil, dust, fingerprint oil, and sand. The same 414 LIBS spectra used in the whole spectra model were used for the new model. According to the RMSECV for the explosives class, the optimal number of latent variables is 30 latent variables. We collected ~3800 LIBS spectra of residues on car panels to test against the model, listed in Table 2. The TPR was 98% for 908 explosive

Table 2. Number of Samples in Training and Validation Sets Used for Classifying Residues on Car Panels

	# in Whole Spectra Model	# in Whole Spectra Test Set	# in Ratios and Intensities Model	# Ratios and Intensities Test Set #1	# in Ratios and Intensities Test Set #2
RDX	69	140	69	603	186 ^a
TNT	25	70	25	305	-
Blank	70	140	70	638	200 ^a
Lubricant oil	70	140	70	639	200 ^a
Dust	60	120	60	538	-
Fingerprint oil	60	120	60	540	-
Sand	60	120	60	521	-
Comp-B	-	-	-	-	331
Diesel fuel	-	-	-	-	593

^aOn second black car panel and light green car panel.

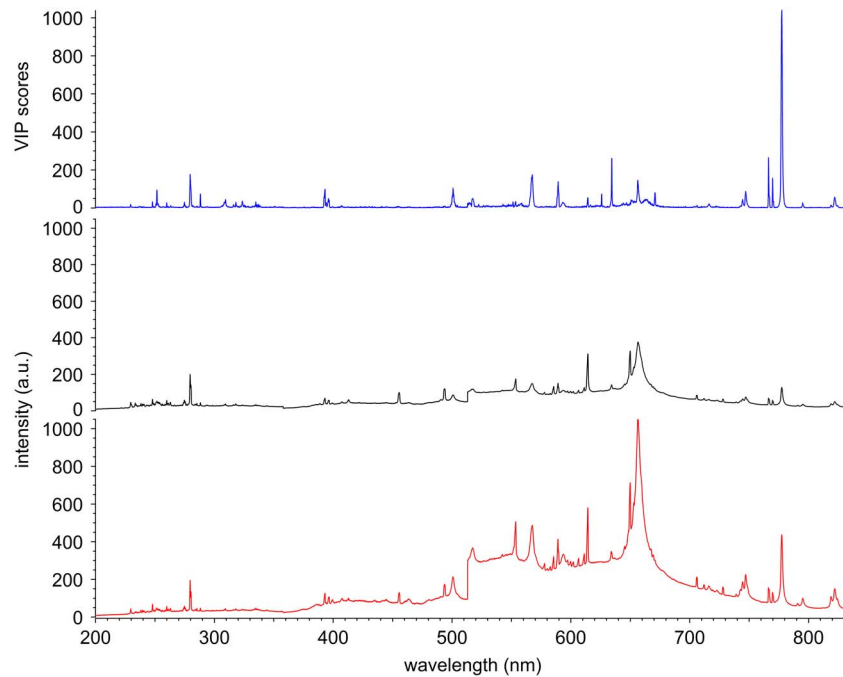


Fig. 7. (Color online) LIBS spectra of RDX on black car panel (bottom) and black car panel (middle) compared to the VIP scores of the explosive class (top) from the whole spectra PLS-DA model.

Table 3. List of Atomic Emission Intensities and Ratios Used as Variable Inputs for PLS-DA Model

C 247	C_2/N	$N/(C + C_2 + CN + H)$	CN/N sum
C 833	C_2/H	$N/(C + CN + H)$	CN/O sum
C_2 516	C_2/N	$N/(C + C_2 + H)$	H/N sum
CN 384	C_2/O	$(O + N)/(C + CN + H)$	H/O sum
CN 385.2	CN/H	$(O + N)/(C + C_2 + H)$	N/O sum
CN 385.8	CN/N	C sum	$(O + N)/(H + C)$ sum
CN 386	CN/O	C_2 sum	$(O + N)/(C + C_2 + CN + H)$ sum
CN 388	H/N	CN sum	$(C_2 + N)/(CN + C)$ sum
H 656	H/O	H sum	$C/(C_2 + O)$ sum
N 742	N/O	N sum	$(O + CN)/C$ sum
N 744	$(O + N)/(H + C)$	O sum	$(N + CN)/C$ sum
N 747	$(O + N)/(C + C_2 + CN + H)$	C sum norm	$(N + C)/CN$ sum
O 777	$((C_2 + N)/(CN + C))$	C_2 sum norm	$N/(CN + O)$ sum
N 818	$C/(C_2 + O)$	CN sum norm	$(O/N)/(H/C)$ sum
O + N 822	$(O + CN)/C$	H sum norm	CN/(N/C) sum
O + N 824	$(N + CN)/C$	N sum norm	$O/(C + C_2)$ sum
C 247 norm	$(N + C)/CN$	O sum norm	$O/(C + CN)$ sum
C_2 516 norm	$N/(CN + O)$	1/C sum	$O/(C + CN + C_2)$ sum
CN 388 norm	$(O/N)/(H/C)$	1/ C_2 sum	$O/(N + CN)$ sum
H 656 norm	CN/(N/C)	1/CN sum	$N/(C + C_2)$ sum
N 747 norm	$C_2/(O/C)$	1/H sum	$N/(C + CN)$ sum
O 777 norm	$O/(C + C_2)$	1/N sum	$N/(C + CN + C_2)$ sum
1/C 247	$O/(C + CN)$	1/O sum	$O/(C + H)$ sum
1/ C_2 516	$O/(C + CN + C_2)$	C/C_2 sum	$O/(C + CN + H)$ sum
1/CN 388	$O/(N + CN)$	C/CN sum	$O/(C + CN + C_2 + H)$ sum
1/H 656	$N/(C + C_2)$	C/H sum	$O/(C + C_2 + H)$ sum
1/N 747	$N/(C + CN)$	C/N sum	$N/(C + H)$ sum
1/O 777	$N/(C + CN + C_2)$	C/O sum	$N/(C + C_2 + CN + H)$ sum
C/ C_2	$O/(C + H)$	C_2/CN sum	$N/(C + CN + H)$ sum
C/CN	$O/(C + CN + H)$	C_2/H sum	$N/(C + C_2 + H)$ sum
C/H	$O/(C + CN + C_2 + H)$	C_2/N sum	$(O + N)/(C + CN + H)$ sum
C/N	$O/(C + C_2 + H)$	C_2/O sum	$(O + N)/(C + C_2 + H)$ sum
C/O	$N/(C + H)$	CN/H sum	$C_2/(O/C)$ sum

Table 4. Classification Results of Residues on Car Panels Using Various Validation Sets

	TPR	FPR
Whole spectra test set	99.5%	1.9%
Ratios and intensities test set #1	98%	2.7%
Ratios and intensities test set #2	84%	2.5%
Fused probability results	97%	0.16%

samples and the FPR was 2.7% for 2876 non-explosive samples. These are similar to the results obtained from the whole spectra model, except that we know the variables that are contributing to the classification are due to the emission intensities and ratios of the constituent elements of the explosive. We further tested this model by collecting LIBS spectra from sample types not used to construct the model. We applied the explosive composition-B and diesel fuel to the seven car panels. In addition, we added RDX and lubricant oil to two different car panels, a second type of a black car panel and a light green car panel. The second test set was tested against the ratios and intensities model using 40 latent variables. The FPR for the second test set consisting of substrates not included in the model was similar to the first test set; however the TPR was slightly lower. All of the TPR and FPR for the test sets described in this section are displayed in Table 4.

C. Fusion of Classification Probabilities

We have previously explored the idea of fusing the probability data generated from one model with probability data generated from a different model [21,24]. In this case, we generated two sets of probabilities from an identical validation sample set by

testing against the whole spectra model and the ratios and intensities model. Then, we multiplied the probabilities from each model for a particular sample together. The new “fused” probability was then used to determine if the sample belongs to the explosive class. The “fused” probability threshold for being classified as an explosive is 0.56 (0.75×0.75). The sample set includes representatives of each of the residue and car panel combinations. There are a total of 156 explosive samples and 631 non-explosive samples. In Figs. 8(a) and 8(b), the probability that a sample belongs to the explosive class is displayed for the whole spectra model and the ratios and intensities model, respectively. In Fig. 8(c), the fused probability for each sample belonging to the explosive class is displayed. It is readily apparent that the number of false positives is greatly reduced. This is a result we have observed in other studies of fusing probabilities from different models. The results are displayed in Table 4. The FPR improves by an order of magnitude from 1.9% to 0.16%.

4. Discussions and Conclusions

The seven car panels were successfully classified based on color, 209 out of 213 test samples, using LIBS spectral data as variable inputs for a PLS-DA model. Using VIP scores, we showed that the classification result was based on the elemental composition of the car panels. More importantly, we have demonstrated that LIBS and multivariate analysis can be used to classify residues as explosive or non-explosive on the painted car surfaces despite the potential interference from constituent elements present in the paint. Two PLS-DA models were constructed: one used the whole spectra and the other

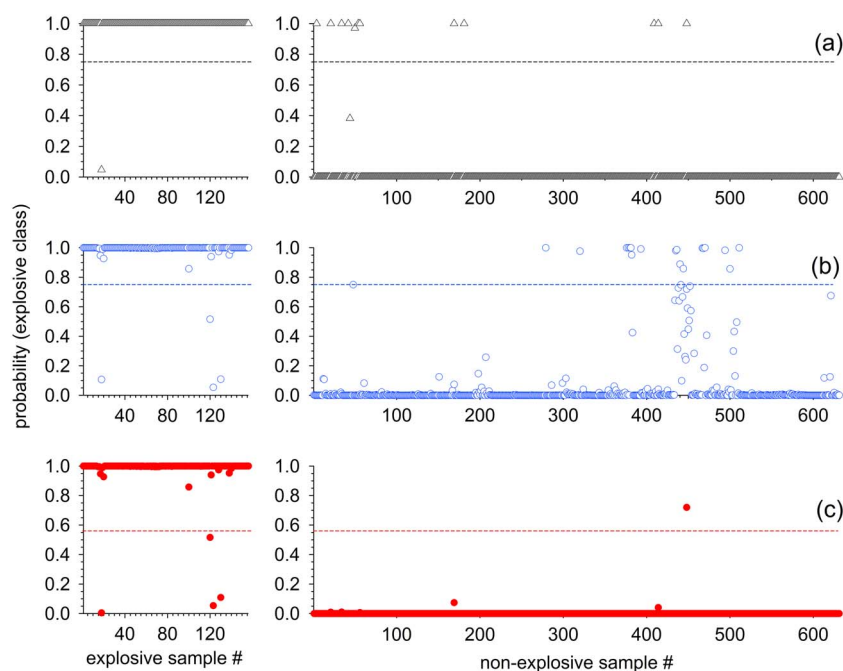


Fig. 8. (Color online) The probability that a test sample belongs to the explosive class determined from the PLS-DA (a) whole spectra model, (b) ratios and intensities model, and the (c) fused probabilities from the whole spectra model and ratios and intensities model.

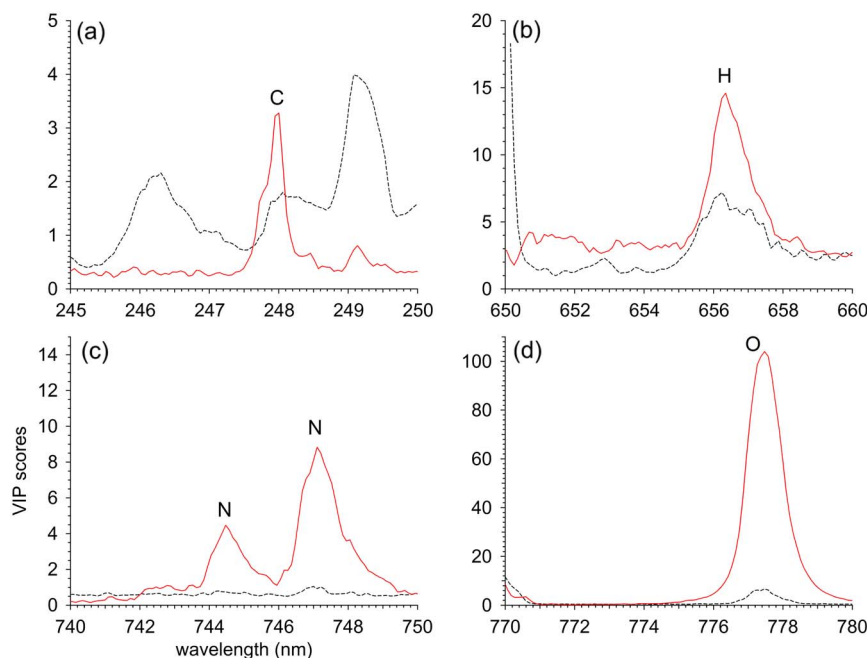


Fig. 9. (Color online) VIP scores of blank car panel class (dotted) and explosive class (solid) in spectral regions containing explosive constituent elements (a) carbon, (b) hydrogen, (c) nitrogen, and (d) oxygen.

used atomic intensities and ratios of the constituent elements, i.e., carbon, hydrogen, nitrogen, and oxygen as the variable inputs. For both of these models, the model classes were based on the residue type, not the car panel color. In Fig. 9, VIP scores from the model based on car panel color and the VIP scores from the whole spectra model based on residue type are compared. The VIP scores of the carbon (248 nm), hydrogen (656 nm), oxygen (777 nm), and nitrogen (746 nm) atomic emissions contribute more to classification in the explosive class than in the car panel class.

Using the preselected atomic emission intensities and ratios as variable inputs has two major advantages: (i) the variables responsible for classification as an explosive are all due to the constituent elements (C, H, N, and O) instead of elements due solely to the car panel substrate, and (ii) significantly less computer processing is needed to create PLS-DA models and test them using 132 variables compared to the 8000+ variables used in the whole spectra model. An additional test set that included samples not used to construct the model was tested against the ratio and intensities PLS-DA model. The TPR was lower, especially for the RDX on the light green panel, but the FPR was about the same. Since the RDX on the light green car panel had the lowest TPR of 78%, a future model might incorporate samples containing residues with light green car panels. A new independent test set of LIBS spectra would be collected to validate the new model.

Previous fusion techniques have focused on using spectral information from two orthogonal techniques such as LIBS and Raman, but this approach can lead to complicated experimental configurations

[7,25,26]. In this work, we demonstrated that building two different PLS-DA models based on the same set of LIBS spectra and subsequently fusing the results from the test data set decreases the FPR for explosive residues on painted surfaces. Decreasing the FPR is essential for applying detection techniques to rarely occurring events. The range and scope of the application, the types of samples being analyzed, the limits and boundaries of the model, and the method of data collection must all be clearly defined in order to fully realize a predictive classification model for successful standoff LIBS residue classification.

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